Guidelines for Safe Storage and Handling of Reactive Materials
by Center for Chemical Process Safety
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Chemical Reactivity Hazards

This chapter gives a systematic overview of chemical reactivity hazards. It will enable the user to answer the questions

What kind of reactivity hazards are posed?

The chemical process industry by nature involves chemical reactions, the production of reactive chemicals and intermediates, and the handling of reactive materials. Most chemicals handled in the industry are not unstable or reactive under normal storage conditions without a strong initiator; however, the reaction of some materials is easily initiated with only a slight deviation from normal conditions, releasing sufficient energy to cause a hazardous event. Reactive chemicals and uncontrolled chemical reactions are often described using various descriptive adjectives such as *unstable, shock-sensitive, vigorous, violent, runaway,* and *explosive.*

Accident and Postaccident Concerns

Potential reactive chemical accidents include fires, explosions, and the generation and release of toxic materials. Reactive chemical incidents have resulted in the loss of hundreds of lives and many millions of dollars in property. Perhaps the most notable reactive chemical incidents are those that are now known merely by the location of their occurrence; namely, the Bhopal methyl isocyanate release and the Seveso dioxin release (documented in Marshall, 1987 and elsewhere).

Reactivity hazards may continue to exist after an incident has occurred and mitigation efforts are underway. Water-reactive materials such as aluminum alkyls, for example, can pose particularly difficult fire-fighting problems. Reactive metals such as sodium and metal hydrides also preclude the use of carbon dioxide or halogenated extinguishing agents. Many reactive materials are thermally unstable and can decompose rapidly if involved in a fire situation. Some reactive chemicals can cause spontaneous combustion in absorbents used for spill control. These examples illustrate the necessity for thorough analysis and careful

design of systems to identify, contain, and control reactive chemicals and respond to reactive chemical incidents.

1.1. Framework for Understanding Reactivity Hazards

In order to identify reactive chemical hazards in a storage or handling facility systematically, a structured understanding of reactivity hazards is important. To this end, an overall framework for identifying reactive chemical hazards is presented in Section 1.2.1, along with brief descriptions of the types of hazards encountered within the given framework. In Section 1.2.2, some fundamentals of chemical reactivity are reviewed in the context of how both thermodynamic and kinetic factors affect reactive chemical systems. The common concept of "runaway reactions," which cuts across many types of reactivity hazards, is discussed in Section 1.2.3. Initiators of reactive chemical incidents are examined in Section 1.2.4.

1.1.1. Grouping of Reactivity Hazards into General Categories

Reactive materials can be grouped into several general categories, as shown in Table 1.1 and described below. While there is some overlap between the categories and subcategories presented here, they nevertheless can serve as a useful framework for understanding the range of reactivity hazards presented by industrially important chemicals.

Table 1.1 divides reactive chemicals into two major groups; namely, those that "**self-react**" and those that **react with other materials.** Each of the common types of reactive materials, such as pyrophoric and shock-sensitive materials, are discussed below within this framework. Those items discussed in detail in this book are shaded in Table 1.1.

Self-Reactive Materials

Reactive materials that are capable of self-reaction will react in one or more of three ways: they will *polymerize*, or form more complex molecules by polymerization-type mechanisms; *decompose*, or break down into simpler molecules such as water and nitrogen; and/or *rearrange* to form variants on the same basic chemical structures or formulas.

Polymerizing compounds are often monomers that self-react, often in the presence of a catalyst, to form polymers or other similar larger, more complex molecular structures by chaining, crosslinking, or similar reactions. Polymerization reactions are generally self-sustaining once initiated, and often highly exothermic. In addition to the heat of reaction, off-gases from the reaction can also pose a significant overpressurization hazard.

Decomposing materials have chemical structures that are relatively unstable and break down easily. Decomposing materials include shock-sensitive and thermally decomposing compounds.The decomposition of a *shock-sensitive*

TABLE 1.1
Reactivity Hazard Types

<table>
<tr><th colspan="6">REACTIVE MATERIALS</th></tr>
<tr><th colspan="3">Self-Reactive (Unstable)</th><th colspan="3">Reactive with Other Materials</th></tr>
<tr><th>Polymerizing</th><th>Decomposing</th><th>Rearranging</th><th>Oxygen-reactive</th><th>Water-reactive</th><th>Nitrogen-Reactive</th></tr>
<tr><td rowspan="4"></td><td>Shock-sensitive</td><td>Isomerizing</td><td>Pyrophoric</td><td>Class A</td><td>Reactive with Metals</td></tr>
<tr><td rowspan="3">Thermally decomposing</td><td rowspan="3">Disproportionating</td><td>Flammable</td><td rowspan="3">Class B</td><td>Oxidizing/ Reducing</td></tr>
<tr><td>Combustible</td><td>Acidic/Basic</td></tr>
<tr><td>Peroxide former</td><td>Toxics; Others</td></tr>
<tr><td>Section 1.2</td><td>Section 1.3</td><td>Section 1.4</td><td>Section 1.5</td><td>Section 1.6</td><td>Sections 1.7, 1.8</td></tr>
</table>

NOTES: Only the shaded categories are treated in detail in these guidelines. Section numbers indicate text sections where categories are discussed. Many reactive materials such as 1,3-butadiene fall into two or more categories. Subcategories within the categories of Decomposing, Rearranging, Oxygen-reactive, and Water-reactive are listed in approximate order of decreasing reactivity.

material can be initiated by a sudden input of mechanical energy. This "shock" can be generated by a number of different mechanisms, such as by the impact of a dropped weight or by hydraulic shock. The decomposition reaction for shock-sensitive materials generally has a relatively small activation energy (discussed in Section 1.2.2), such that the mechanical energy input is sufficient to initiate the reaction, and the reaction is exothermic enough to be readily self-sustaining once initiated.

Thermally decomposing materials require a minimum thermal input before a significant decomposition reaction occurs; however, once initiated, the material may decompose at an accelerating rate until it proceeds at an uncontrollably high rate of reaction ("runaway" decomposition reaction).

Peroxides are a subset of decomposing materials that deserve special mention because of their industrial importance. Peroxides are chemical compounds that contain the peroxy (–O–O–) group. Peroxides can be considered as derivatives of hydrogen peroxide (HOOH), with organic and/or inorganic substituents replacing one or both hydrogens. Some peroxide formulations are shock-sensitive, but most are thermally decomposing. Many organic peroxides have particular stability problems that make them among the most hazardous of industrial chemicals.

Rearranging materials may undergo reactions in which their chemical bonds or chemical structure is simply rearranged. Isomerizing and disproportionating chemicals are part of this group.

Reactive with Other Materials

Substances may be stable by themselves, but will readily react with one or more common materials such as atmospheric oxygen, water, or metals. While quantitative chemical reactions such as oxidation–reduction and acid–base reactions, as well as biological reactivity (toxicity), are also in this category, they will not be treated in detail in this book. Likewise, materials that are only flammable or combustible are not given detailed treatment. They are not generally considered "reactive" chemicals, and the storage and handling of flammable and combustible materials are covered extensively in publications by such organizations as the National Fire Protection Association and the American Petroleum Institute.

Oxygen-reactive materials may be further broken down into pyrophoric, low-temperature autoignition, flammable, combustible, and peroxide-forming substances.

Pyrophoric materials are highly reactive with atmospheric oxygen and/or humidity. The energy released by the oxidation and/or hydrolysis reaction is great enough to cause ignition of the material after only a brief delay.

Materials exhibiting *low-temperature autoignition* require an above-ambient temperature but well below the normal autoignition temperature (AIT) range for self-sustained combustion in air to be initiated. A notable example is carbon disulfide, which has an AIT around 212°F (100°C).

Flammable and *combustible* materials will burn in air at normal or elevated temperatures but require an ignition source to start the oxidation reaction. "Combustible" is the more general of the two terms, and can refer to any solid, liquid, or gaseous substance that will burn in air. When applied to liquids, it generally refers to those liquids having a closed-cup flash point of 100°F (37.8°C) or greater. Flammable liquids are those having a closed-cup flash point below 100°F (i.e., that can be easily ignited at normal ambient temperatures). NFPA 321 (1991) gives more specific information on the classification of combustible and flammable liquids.

A *peroxide former* is a material that slowly reacts with air without an ignition source ("autoxidation") to form a peroxidic compound. Peroxide formers pose longer-term hazards; nevertheless, these hazards are significant in that the reaction products can include highly unstable organic peroxides. A few inorganic compounds, such as potassium and the higher alkali metals and sodium amide, can autoxidize and form peroxides or similarly hazardous reaction products.

Water-reactive materials are another category of reactive materials that will react with water, more or less violently. In addition to the problems surrounding the exclusion of all water in storage and handling operations, water-reactive materials also pose obvious fire-fighting difficulties.

1.1.2. Key Parameters That Drive Reactions

The reactions associated with the types of reactive materials outlined above have several governing principles in common. Thermodynamic, kinetic, and physical parameters are important in determining the potential for, and nature of, uncontrolled reactions. Table 1.2 summarizes these parameters.

Smith (1982) provides a good summary of both the objective and the difficulties of obtaining the proper thermodynamic and kinetic data:

> The primary objective of thermokinetic studies is to determine a temperature ceiling below which one can safely work. In principle, it is not possible to state such a temperature because the reaction-rate curve does not simply decrease to zero as temperature decreases. In fact, there is no [fundamental] physical quantity such as the decomposition or onset temperature, except for decompositions that start at melting points.
>
> The heat generation rates of specific samples depend on temperature, degree of conversion, and often, previous thermal history. The onset of a particular heat release rate will be detected at widely different temperatures, depending on the sensitivity of the instrument used.

To be able to obtain and interpret the necessary thermokinetic data properly, a basic understanding of reactivity parameters is necessary. Stepwise assessment of reactivity hazards by theoretical calculations and physical testing is detailed in Chapters 3 and 4.

TABLE 1.2
Parameters of Exothermic and Runaway Reactions[a]

THERMODYNAMIC PARAMETERS
Reaction energy
Adiabatic temperature increase
Specific quantity of gas generated
Maximum pressure in a closed vessel
KINETIC PARAMETERS
Reaction rate
Rate of heat production
Rate of pressure increase in a closed vessel
Adiabatic time to maximum rate
Apparent activation energy
Initial temperature of detectable exothermic reaction
PHYSICAL PARAMETERS
Heat capacity
Thermal conductivity
Surface-to-volume ratio

[a]After Smith, 1982.

Thermodynamic Parameters

One of the key measures of the magnitude of a reactive chemical hazard is the overall energy that *could* be released in the event that a reaction does take place. This potential energy release is known by various terms, depending on the type of reactive system. For self-reactive chemicals, it is the *heat of polymerization, heat of decomposition,* or *heat of rearrangement.* For systems with more than one reactant, the potential energy release is the *heat of reaction.* (For combustion reactions, the heat of reaction is further specified as the *heat of combustion.*)

The potential energy release is calculated as the difference between the total heat of formation of the product(s) and the total heat of formation of the reactant(s). Heats of formation for many individual chemicals can be obtained from standard chemical engineering and thermodynamics references (e.g., Perry and Green, 1984, 3-147ff). Most reactive chemical systems of concern for safe storage and handling considerations have a greater total chemical energy "content" in the initial reactant(s) than in the products; consequently, energy is released when the reaction occurs, the reaction is termed *exothermic,* and the reaction energy such as the heat of decomposition or the heat of combustion has a negative value. (The international convention of positive values for energy absorption and negative values for energy release is used here.)

The liberated thermal energy can cause pressure generation by vaporization and/or gas generation, ignition of nearby materials, acceleration of chemical reactions, burns to nearby personnel, etc., and thus is the major concern in safely storing and handling reactive chemicals. This reaction energy parameter can be used, for example, to calculate the adiabatic temperature rise for a reaction, which can be combined with the specific volume of the gas generated by the reaction to calculate a maximum internal pressure that can be developed inside a storage tank or other containment.

A highly exothermic reaction usually indicates a very energetic and reactive material or combination of materials. For example, as a rule of thumb, an individual compound is apt to be "explosive" if its heat of decomposition is greater than about 100 cal/g (420 kJ/kg). However, the spontaneity or irreversibility of a reaction is determined by both the reaction energy (enthalpy) and the tendency of a system to go from an ordered state to a more disordered state (increased entropy). A measure that combines enthalpy and entropy is the *Gibbs free energy,* calculated as follows for a compound:

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

where ΔG_f is the Gibbs free energy of formation of the compound in J/mol, DHf is the heat of formation of the compound in J/mol, T is the absolute temperature in Kelvin, and ΔS_f is the entropy of formation of the compound in J/mol·K. The more negative the Gibbs free energy of reaction, the greater the tendency of the material(s) to react spontaneously and irreversibly at the conditions of interest (such as standard state). Stull (1977, 10–13) gives a basic discussion of entropy

and Gibbs free energy. The heat of reaction is likely used more than the Gibbs free energy in thermodynamic evaluations because it is a measure of the total energy available if the reaction occurs.

One other commonly used thermodynamic term used in identifying reactive materials needs to be noted. Self-reactive materials that have a significantly positive heat of formation are often called *endothermic compounds,* since these substances require energy input for their formation from constituent elements. For example, acetylene gas has a heat of formation ΔH_f of +54.2 kcal/g-mol. This 54.2 kcal/g-mol would be released to the environment as thermal energy upon decomposition of acetylene to its elements. Consequently, endothermic compounds tend to be relatively unstable, unless the entropy change for the decomposition reaction is significantly positive. This terminology can lead to confusion, since the decomposition of an endothermic compound is an *exothermic* or heat-releasing reaction.

Kinetic Parameters

The basic kinetic variable that must be considered in reactive chemical systems is the **reaction rate.** The reaction energy (e.g., heat of decomposition) and the reaction rate together determine the rate of heat release that must be dealt with in the control of reactive chemical systems. The reaction rate, in turn, is a function of both temperature and reactant concentrations:

$$\text{Rate} = k_T \cdot [\text{concentration-dependent term}]$$

where k_T is the temperature-dependent "rate constant." In most chemical reactions, the temperature dependence of the reaction rate is of the form shown in Figure 1.1. This particular temperature dependence is commonly characterized using the empirical Arrhenius relationship:

$$k_T = e^{-e_a/RT}$$

where A is the Arrhenius frequency factor (usually assumed to be independent of temperature), E_a is the activation energy of the reaction, R is the gas constant, and T is the temperature. More detailed treatment of reaction rate parameters can be found in texts such as Levenspiel (1972) and Carberry (1976).

The activation energy can be considered as the energy input or "barrier" required by a reactive system to initiate a particular chemical reaction, as illustrated in the energy diagram of Figure 1.2. This figure also shows the interrelationship between the kinetic parameter of activation energy and the thermodynamic factor of reaction energy (heat of reaction). The most hazardous reactive systems have low activation energies (and therefore easily initiated) and highly negative heats of reaction (and therefore capable of releasing large amounts of energy). Reactive chemical types are qualitatively tabulated as to their expected activation energy and reaction energy in Table 1.3 for self-reactive chemicals and Table 1.4 for systems involving more than one reactant.

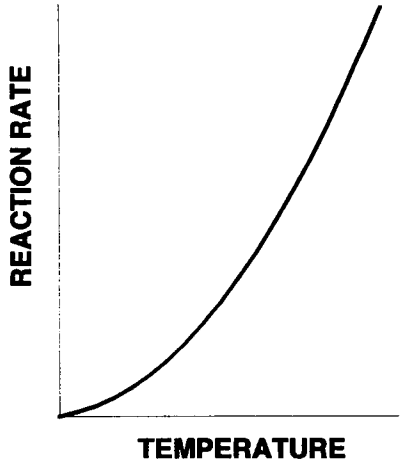


FIGURE 1.1. **Basic Temperature Dependence of Reaction Rate**

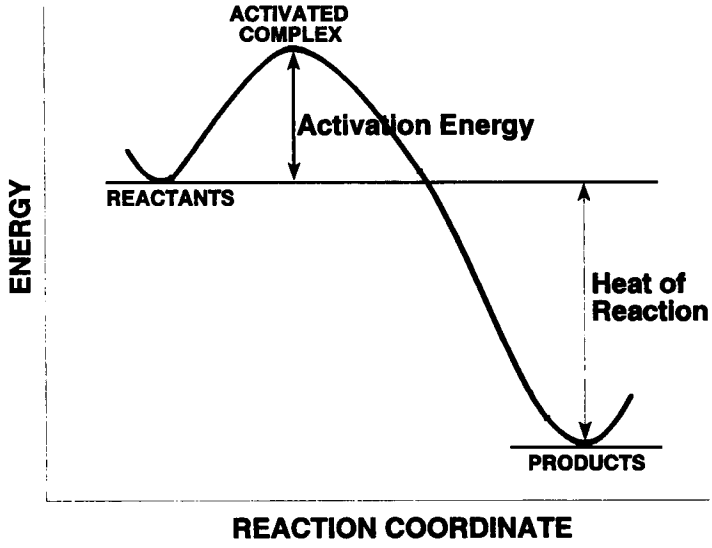


FIGURE 1.2. **Activation Energy and Heat of Reaction.**

TABLE 1.3
Thermokinetic Matrix: Self-Reactive Chemicals

Heat of Polymerization, Decomposition, or Rearrangement	*Activation Energy (can be reduced by presence of catalyst)*		
	Near Zero	*Low to Medium*	*High*
Highly Negative (exothermic)	Unstable intermediates and transition forms (spontaneously decompose)	Explosively decompose; initiation by shock or small thermal energy input	Explosively decompose or polymerize; initiation requires a greater shock or thermal energy input
Slightly Negative		Decompose, polymerize, or rearrange with moderate thermal energy input	Decompose or polymerize with fairly high thermal energy input
Zero	Most stable elemental states at standard conditions		
Slightly Positive	Readily decompose or rearrange; proportional to energy input	Decompose or rearrange with moderate thermal energy input	Decompose with considerable energy input

TABLE 1.4
Thermokinetic Matrix: Reactive Mixtures

Heat of Reaction	*Activation Energy (can be reduced by presence of catalyst)*		
	Near Zero	*Low to Medium*	*High*
Highly Negative (exothermic)	Hypergolic mixtures; pyrophoric; Class A water-reactive	Shock-sensitive explosive mixtures; highly flammable	Reactive/combustible/ polymerizing mixtures; initiation requires greater energy input
Slightly Negative		Autoxidizing; Class B water-reactive; slightly flammable	Reactive with significant energy input
Zero	Sum of heats of formation of reactant(s) equal to sum of heats of formation of product(s)		
Slightly Positive	Readily reactive; proportional to energy input	Reactivity takes moderate thermal energy input	Reactivity would take considerable energy input
Highly Positive	Reactivity takes moderate thermal energy input	Reactivity would take considerable energy input	Reactivity would take extreme conditions

NOTE: Qualitative trends rather than absolute categories are indicated. Reactivity will depend on entropy change as well as heat of reaction, and outcome will depend on physical parameters such as heat dissipation to surroundings.

The thermodynamic parameters such as heat of decomposition and heat of reaction can be calculated from literature values for common compounds. However, the kinetic parameters for a given reaction must generally be obtained from physical testing. Measurement of the adiabatic temperature rise as a function of time can yield the activation energy, adiabatic time to a runaway reaction, and maximum rate of pressure rise for a given system; other parameters such as decomposition stoichiometry and vessel fill rate may also need to be addressed. The initial temperature of a reaction system is another important parameter. The initial temperature determines where the system begins along the curve of reaction rate versus temperature. Test methods for determining kinetic parameters are discussed in Chapters 3 and 4.

The reaction rate can be a complex function of the reactant and product concentrations. However, Smith (1982, 81) notes that:

> The assumption of a zero-order kinetic model produces a good approximation of dynamic behavior for most systems. Figure 1.3 shows a first-order decomposition reaction. Note that the self-heat rate starts out as a straight line, but falls off as reactant concentration decreases. We also note from Figure 1.3 that the apparent curvature is drastically reduced when the end-point of the study is defined as maximum rate. With this restriction, we can see why an *n*th-order reaction approaches a zero-order reaction in studies mostly concerned with the reaction up through the maximum rate.

Physical Parameters

The third group of parameters which, in combination with thermodynamic and kinetic parameters, largely determine the future of a reaction system, are the physical parameters: heat capacities of the reactants and products, heats of vaporization, the overall thermal conductivity of the reacting volume and of the containment vessel, and the surface-to-volume ratio of the containment. Based on relationships between these parameters, critical radii or volumes can be determined for various vessel configurations.

How These Parameters Affect Thermal Stability

The thermal stability of a chemical system is the ability of the system to safely remove the heat of an exothermic reaction (either self-reaction or reaction with other materials). This stability is determined by a combination of the thermodynamic, kinetic, and physical parameters, with the kinetic and physical parameters being of most importance. Two outcomes are possible for a system involving an exothermic reaction: the system will either come to a thermal equilibrium between heat generation and heat removal, or the system will spiral upward in temperature. Even very slow heat-evolution rates may lead to dangerous situations if they occur under heat-accumulation conditions. On the other hand, highly exothermic reactions can be safely handled with adequate heat transfer (Smith, 1982).

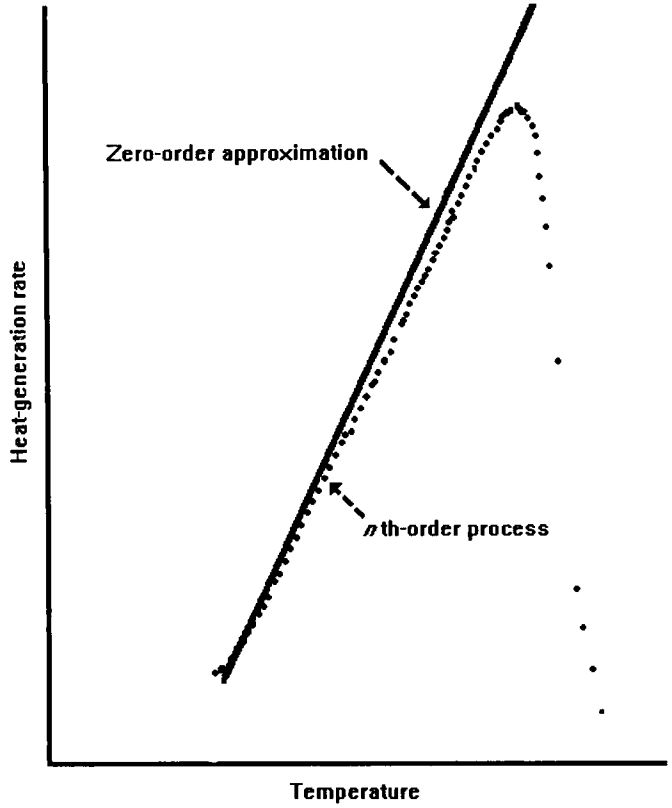


FIGURE 1.3. **Zero-Order Kinetic Model versus Dynamic Behavior of a System** (Smith, 1982)

As seen in the preceding section, the reaction rate, and thus the rate of heat generation, is an exponential function of temperature. The practical rule of thumb that the reaction rate often doubles or even triples for each increase of 10°C in reaction temperature illustrates this strong dependence of reaction rate on temperature. On the other hand, the heat transfer of a system (which is determined by the physical parameters) is a linear or nearly linear function of temperature difference. Hence, as the temperature of a reaction system increases, the heat-generation rate becomes more important than the heat-transfer ability of the system. At some point, called the "temperature of no return" (T_{NR}), the reaction heat can no longer be removed, the system temperature increases exponentially, and a thermal runaway ensues. These relationships are illustrated in the Semenov plot of Figure 1.4. (The heat generation curve flattens out due to consumption of reactant. The actual curve of temperature versus heat generation rate for a given system, such as one involving multiple reactions, may be significantly different than in Figure 1.4.)

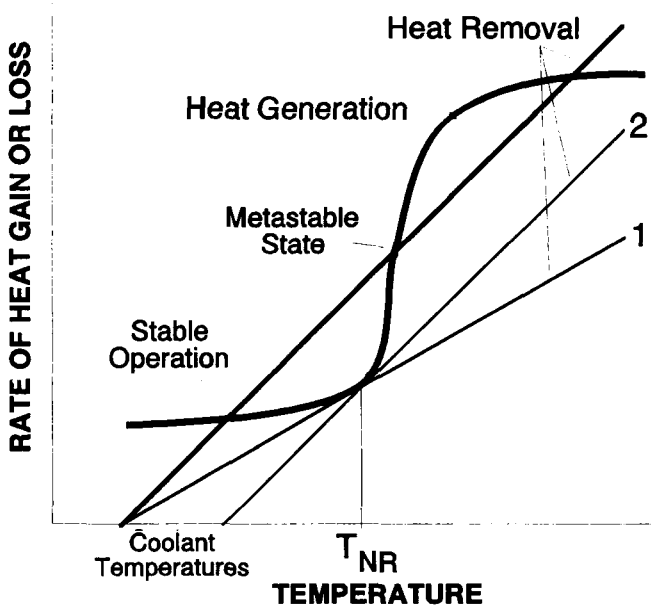


FIGURE 1.4. **Thermal Stability Determined by Heat Generation and Heat Removal**

Thermal runaways occur when the rate of heat generation from a process exceeds the rate of heat loss to the environment from the process container or vessel. The challenge is the determination of the rates of heat loss and heat generation as a function of the system variables. Having a thorough knowledge of the heat generating process, especially early in the reaction, can serve a useful part in helping to elucidate the potential thermal runaway.

The concepts represented in Figure 1.4 are critical to understanding the safe handling of reactive materials. Referring to this figure, there are two ways to affect the thermal stability, or equilibrium, of a system:

- Loss of heat-removal ability, such as by loss of cooling, loss of mixing, or similar deviations, will lower the slope of the heat-transfer line, although the stationary cooling temperature remains the same. If the slope decreases farther than is shown in curve 1, the heat-generation and heat-removal curves will no longer intersect. This is known as the hypercritical state, where heat removal is always less than heat generation. The reaction temperature will rise uncontrollably, creating a thermal runaway.
- The coolant temperature may increase while the heat-removal slope remains unchanged. If this is done, the heat-transfer line moves parallel to itself until it becomes tangential to, and then goes below, the heat-generation line. This situation is represented by curve 2. Even if the two

curves are tangential, a slight increase in the coolant temperature will cause loss of thermal equilibrium. Above this temperature T_{NR} (temperature of no return), thermal equilibrium is not possible, and a runaway reaction must occur.

1.1.3. Types of Runaway Reactions

Most industrially important chemicals that have the potential for a thermal runaway reaction are stored and handled in the liquid phase and have the potential for self-reaction by either decomposition or polymerization. However, autoaccelerating reactions can occur in gaseous, solid, or mixed phases. Reaction mechanisms such as autocatalysis can also lead to uncontrolled autoacceleration of a reaction.

Gas-Phase Runaways

A few storage/handling configurations for gases have the potential for gas-phase runaway reactions when the heat evolved from an exothermic reaction occurring at moderate rates cannot be dissipated sufficiently. For example, runaway has occurred in several instances of regeneration of ethylene dryers using hot ethylene at about 518°F (270°C) and 1000 psia (Britton, 1994). Exposing acetylene and other gases that will decompose at elevated temperatures to fire conditions can initiate a runaway decomposition reaction. Flammable gases mixed with air undergo a "runaway" combustion reaction when the *autoignition temperature* is reached for the particular containment configuration, gas concentration, and initial pressure.

Condensed-Phase Runaways

Runaway reactions involving a solid phase are possible. For example, adsorption of organic vapors in a bed of activated carbon is exothermic, and sufficient heat of adsorption can result in autoignition of the carbon bed if sufficient oxygen is present and heat dissipation is inadequate.

Importance of Coupled Reactions

Fully identifying reactive chemical hazards must include all pertinent reactions. For example, a polymerization reaction might generate sufficient heat to lead to another reaction, say a decomposition reaction, at a higher reaction temperature. Identifying and controlling only the polymerization reaction may lead to inadequate system safeguards against the decomposition reaction. This is particularly important to note when interpreting screening test data. Testing a reactive mixture in a differential scanning calorimeter (DSC) might show just one exotherm. Testing the same mixture in an accelerating rate calorimeter (ARC) might show two exotherms. A highly adiabatic apparatus might show four to five or more different exotherms for the same mixture. Often, the higher exotherm result is gas generation and not just heat evolution.

1.1.4. How Reactive Chemical Storage and Handling Accidents Are Initiated

Many of the underlying causes of incidents and accidents that have involved unexpected violent chemical reactions are related to a lack of appreciation of the effects of physical and chemical factors on the kinetics of practical reaction systems (Bretherick, 1986).

Accidents involving reactive chemicals are initiated by a number of factors arising from within the storage and handling containment, and from the environment outside the containment. In general, these factors affect reactivity by

- reducing the apparent activation energy E_a
- adding energy to the system (i.e., helping the system obtain the activation energy)
- changing the reaction path
- reducing heat loss to the surroundings

or a combination of the above.

How Storage and Handling Conditions Affect Reactivity Containment

Important factors in preventing the types of runaway reactions discussed previously are mainly related to the control of reaction velocity to as slow a rate as possible without changing the reaction path, as well as keeping the temperature within suitable limits. This may involve such considerations as adequate **cooling capacity** in both liquid and vapor phases of a reactive chemical storage and handling system. Cooling can be impacted by the use of **solvents** as diluents, changing the **viscosity** of the reactive medium, changing **agitation** in the storage vessel, and control of vessel **pressure** (Bretherick, 1990). Loss of agitation or loss of cooling has often been the main contributory factor in cases where inadequate temperature control has caused exothermic reactions (normal, polymerization, or decomposition) to run out of control. The converse, the addition of **heat** (energy) to a system, may either initiate or accelerate a chemical reaction by providing the energy input to overcome the apparent activation energy of the reactive system, thus increasing the reaction rate.

The **ratio of volume to surface area** for a system will impact the flow of excess energy out of the system. This in turn will affect the temperature of the system over time. As a result, some substances or mixtures that are not hazardous in small amounts may turn out to be hazardous when the quantity of material is increased. Accordingly, the scaling up of a storage system should take these factors into account.

To save some of the expense of heating or cooling, vessels are often **insulated**, particularly during long-term hot storage. Materials of limited thermal stability, or which possess self-heating capability, are potentially hazardous in such near-adiabatic systems if insulation is used (Bretherick, 1990, xxiv). Also, if a

reactive material leaks into insulation, similar self-heating and ignition at the hot spot may occur.

Some reactions have a significant **induction time**, which may lead to a false sense of security. Even with the use of inhibitors, a self-accelerating reaction may still only be delayed and not prevented. In addition, some inhibitors change the path of the reaction to one that may be even more hazardous (Cardillo and Nebuloni, 1992).

Consequently, **prolonged storage** is of concern in any case. The same is true for pressurized systems or systems where **fresh metal surfaces** or metal powder may be produced. Catalysts, usually present in storage/handling situations as **contaminants**, effectively reduce the energy of activation, thus increasing the rate of reaction or changing the reaction path (Bretherick, 1990, xxii).

Mechanical shock can be sufficient to provide the activation energy for the decomposition of some highly unstable materials. **Friction** between materials in any phase, especially during transfer operations, may either increase the local temperature of the materials or lead to the development of a static electric charge. **Viscosity** can contribute via friction to static charge build-up and can also help produce hot spots in a reactive material by reducing convective heat transfer. Accumulation of **static electricity** and release of the energy as an electrostatic discharge is a well-documented ignition source.

External heat sources such as from **hot tapping** can initiate a thermal decomposition reaction. Sufficient heat can also be produced by process equipment, such as a **dead-headed** pump (particularly when blocked in on both the inlet and outlet of the pump) or a **hot seal**; even the pumping of reactive material around during standby operations, such as through a pump recirculation line, can gradually increase the temperature of the material.

Any significant **electromagnetic radiation** with such a wavelength distribution that it can be absorbed by the system, or can heat up the system indirectly via its containment, can pose an initiation hazard. Ultraviolet radiation is energetic enough to provide the activation energy for self-reaction of some substances.

Light can form free radicals that can initiate an uncontrolled polymerization reaction. **Direct sunlight** is capable of creating areas where temperature is significantly above ambient. For example, a fire occurred in a material whose autoignition temperature was much higher than ambient temperature. The material was stored on pallets outside on asphalt during summer. The material was heated by solar energy, then self-heated until it ignited the wooden pallets it was stored on (Englund, 1991).

For chemicals that are reactive with air, an **inert atmosphere** may be required to ensure stability. A loss of inerting, or a leak or vacuum break, may lead to an uncontrolled reaction in such reactive systems.

Hazards associated with certain **materials of construction**, such as the use of aluminum in an environment with halogenated hydrocarbons, have also been identified (Cardillo and Nebuloni, 1992).

Autoignition Temperature

In addition to the above considerations, the autoignition temperature (AIT) for many reactive chemicals is highly dependent upon pressure. Autoignition temperatures tabulated for many materials are only accurate for the pressure and configuration of the test conditions, but can be used as approximations for other configurations. Increased pressure will usually lower the autoignition temperature (Figure 1.5).

The hazards of cool flames should also be noted. *Cool-flame ignition* is a relatively slow, self-sustaining, barely luminous gas-phase reaction of a material or its decomposition products with air or another oxidant (NFPA 325M, 1991). Cool flames often cause temperature increases of about 150°K. Transition from the slow combustion of cool flames to hot-flame ignition may occur under certain conditions in process equipment.

Figure 1.5 shows the behavior of a material (e.g., an ether) that exhibits cool-flame ignition behavior. At 1 atm pressure, only slow combustion, with a cool flame, is found up to the autoignition temperature (AIT), at which point a rapid, hot-flame combustion reaction is initiated. In this case, the lowest *cool-flame reaction threshold* (CFT) is much lower than the AIT. At a higher initial pressure (such as 2 atm in Figure 1.5), it is possible to enter the ignition region at a temperature even lower than the ambient-pressure CFT (CCPS/AIChE,

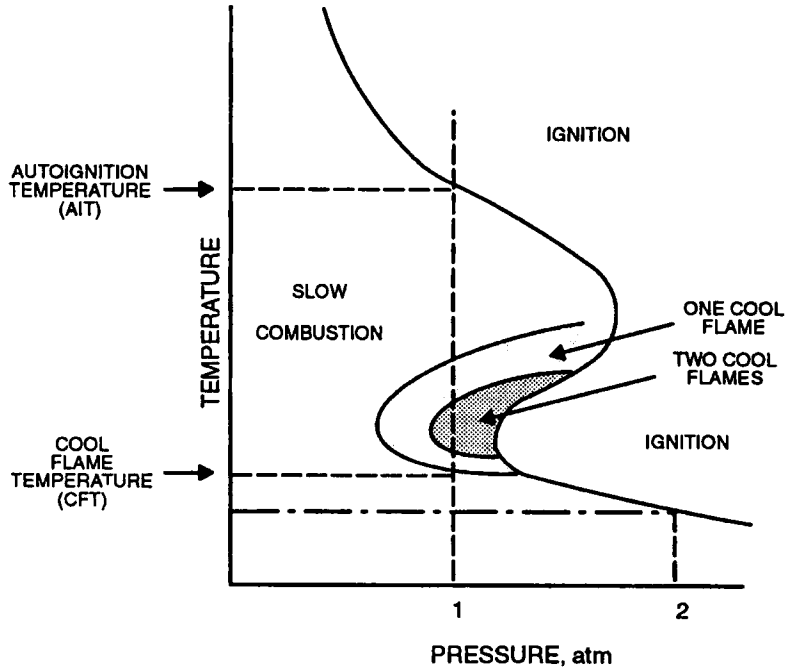


FIGURE 1.5. **Schematic Autoignition Temperature–Pressure Diagram**

1993, 323). With reference to Figure 1.5, if the cool flame region were entered in a closed vessel initially at 1 atm pressure, the increased temperature and pressure from the cool-flame reaction could shift the entire system into the hot-flame ignition region. Consequently, in a closed vessel, a cool flame could increase the pressure of the vessel to the point that the autoignition temperature could be attained.

1.2. Self-Reactive Polymerizing Chemicals

Some chemicals present a hazard due to their ability to react to form larger molecules in a self-sustaining polymerization reaction. The reaction is exothermic, often producing significant quantities of off-gas, with the heat and/or gas generation being capable of overpressurizing storage and handling equipment and possibly resulting in a vessel rupture explosion. Some high-volume industrial chemicals that are self-polymerizing are listed in Table 1.5.

Undesired polymerization reactions can usually be prevented or controlled by the addition of reaction inhibitors, by controlling the bulk temperature of the material, or by controlling the pressure of the system. However, contamination of materials subject to polymerization, as well as external heating from fire exposure, can overwhelm these safeguards. Consequently, emergency response to fires and uncontrolled situations involving polymerizable chemicals must be planned carefully.

1.2.1. Thermal Instability

Materials that are *thermally unstable* will, at some specific temperature (usually above ambient), undergo some type of potentially hazardous reaction such as

TABLE 1.5
Some Self-Polymerizing Chemicals

Acrylonitrile	Propylene
1,3-Butadiene	Propylene Oxide
Ethylene	Styrene
Ethylene Oxide	Vinyl Acetate
Methacrylic Acid	Vinyl Chloride
Methyl Methacrylate	

polymerization, decomposition, or rearrangement, with consequent release of energy. In general, the *reaction onset temperature* is reported. The onset temperature is essentially the lowest temperature for which the thermal energy of the system is sufficient for the reaction to proceed at a measurable rate in a given experimental apparatus or process vessel. Tests designed to detect this onset temperature are described in Chapter 3. If known, the *self-accelerating decomposition temperature,* discussed in Section 1.4, is also reported.

Onset temperature is an important concept for reactive mixtures as well. The NFPA *Manual of Hazardous Chemical Reactions* (NFPA 491M, 1991), and *Bretherick's Handbook of Reactive Chemical Hazards* 1990 have information on reactions between specific chemicals, although onset temperatures are generally not reported. In general, onset temperatures are difficult to measure reliably and are frequently difficult to define precisely in complex systems.

1.2.2. Induction Time

Induction time or *induction period* is an important safety consideration in the storage and handling of polymerizable materials, in that inhibitors are often added to monomer storage to prevent the onset of a polymerization reaction. Bretherick (1990, 1636–1637) has a good description of induction period for hazardous reactions:

> In the absence of anything to prevent it, a chemical reaction will begin when the components and any necessary energy of activation are present in the reaction system. If an inhibitor (negative catalyst or chain-breaker) is present in the system, it will prevent the onset of normal reaction until the concentration of the inhibitor has been reduced by decomposition or side reactions to a sufficiently low level for reaction to begin. This [apparent] delay in onset of reaction is termed the *induction period.*

Chemicals and reactive systems exhibiting induction periods, such as Grignard reagents, are listed in the same reference. As illustrated in Figure 1.6, it is not necessary to have an inhibitor present to have an induction period for a given reaction. The induction time τ_2 in Figure 1.6 begins either at the start of the storage time for a material with no inhibitor present or at time τ_1 when all of the inhibitor has been used up.

The induction period can be affected by many variables, such as the presence of impurities, the temperature and pressure history of the contents, and the presence and concentration of inhibitors (Nicolson, 1991). Several means are available to monitor and ensure an adequate inhibitor concentration, such as periodic sampling, temperature or rate of temperature rise measurement, and inhibitor loss-of-flow alarms. Detailed design considerations for polymerizable compounds are given in Section 6.2.

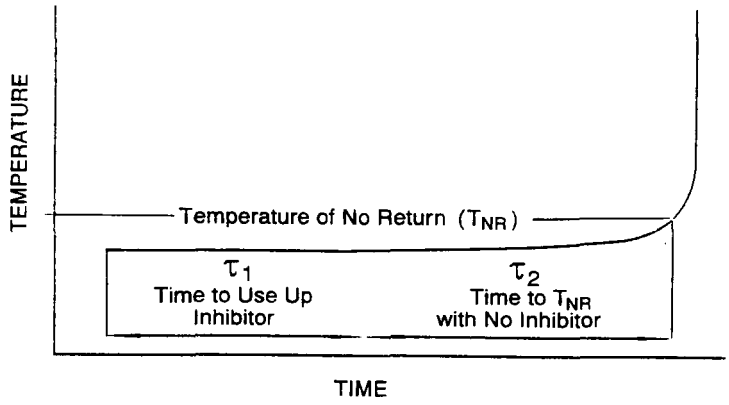


FIGURE 1.6. **Induction Time**

1.2.3. Example

Nicolson 1991 reports that hydroquinone and monomethyl ether of hydroquinone (MEHQ) can be used as inhibitors of methacrylic acid polymerization. However, both hydroquinone and MEHQ require the presence of oxygen to be effective as inhibitors. The oxygen concentration has a great impact on the stability of the monomer. At the right concentrations, oxygen increases the induction period of methacrylic acid. However, peroxide decomposition is associated with the onset of polymerization, with the potential consequence of a violently exothermic polymerization reaction initiated by the peroxide. Note also that needing oxygen to be present for inhibitor activation may be in conflict with inerting requirements, so that a controlled oxygen addition scheme may be necessary.

1.3. Self-Reactive Decomposing Chemicals

$$AB \rightarrow A + B + \Delta$$

A second major group of reactive chemicals are self-reactive by decomposing into smaller molecules, rather than combining together to form larger molecules as in polymerization. Decomposition reactions can liberate large amounts of energy, often with explosive violence. Some decomposition reactions can be initiated by mechanical shock alone, such as by a falling object striking the material; such materials are termed *shock sensitive*. At the other end of the spectrum of decomposing chemicals are those that will decompose after being exposed to an elevated temperature for a period of time; such materials are

termed *thermally decomposing*. Shock and elevated temperature are not the only stimuli that can initiate decomposition reactions; other mechanisms include friction, light, trace contaminants such as rust or metal powders, and trace chemical contaminants such as oxidizing or reducing agents. Elevated pressure may also be important. For example, acetylene has decomposed explosively when faulty pressure control has allowed pressures in acetylene generators and distribution systems to approach 20.3 psig in the presence of moisture (Bretherick, 1990, 231).

1.3.1. Peroxides

One group of industrially important chemicals that has characteristics of both the shock-sensitive and thermally decomposing categories is the *peroxides*, characterized by the oxygen–oxygen single bond. Peroxides can be divided into inorganic peroxides, organic peroxides, and organomineral peroxides, depending on the substituents on either or both sides of the oxygen-oxygen bond.

Peroxides have a specific half-life, or rate of decomposition, under any given set of conditions. A low rate of decomposition may autoaccelerate and cause a violent explosion, especially in bulk quantities of peroxide. These compounds are sensitive to heat, friction, impact, and light, as well as to strong oxidizing and reducing agents.

Some peroxides such as many of the organic peroxides are extremely shock sensitive; other peroxides are quite shelf stable. As a class, organic peroxides are hazardous because of their extreme sensitivity to shock, sparks, heat, or other forms of accidental ignition. Some peroxides that are routinely handled in industry are more sensitive to shock than secondary explosives such as trinitrotoluene (TNT). For this reason, many peroxides are shipped in a diluent; ensuring that the diluent is always present is, therefore, a safety-critical design and operating consideration for such peroxides.

The highly reactive nature of many organic peroxides can be attributed to their having both oxidizing and combustibility properties. Specific recommendations regarding organic peroxides are given in NFPA 43B, *Code for the Storage of Organic Peroxide Formulations* (1993).

1.3.2. Self-Accelerating Decomposition Temperature

An important measurement of the storage stability for potentially unstable materials is the temperature at which an uncontrolled decomposition reaction can be initiated. The following basic description of the self-accelerating decomposition temperature (SADT) is taken from NFPA 49 (1994, 145):

> Certain compounds, such as organic peroxides and [some] swimming pool chemicals, when held at moderate ambient temperatures for an extended period of time, may undergo an exothermic reaction that accelerates with increase in

> temperature. If the heat liberated by this reaction is not lost to the environment, the bulk material increases in temperature, which leads to an increase in the rate of decomposition. Unchecked, the temperature grows exponentially to a point at which the decomposition cannot be stopped or slowed. The minimum temperature at which this exponential growth occurs in a material packed in its largest standard shipping container is defined as the *self-accelerating decomposition temperature.* Self-accelerating decomposition temperature is a measure of the ease in which decomposition occurs under normal storage [shipment] conditions. It is not an indicator of the violence of any decomposition reaction under conditions of fire exposure or contact with incompatible materials.

It should be noted that the SADT only applies to the container size and surface–volume configuration in which the material was tested. UN transportation requirements specify that a material to be shipped must be stable at 55°C for one week. U.S. DOT requires stability at 130°F (54.4°C) for the duration of the shipment. It can be argued that this "duration" could be anywhere from one week to six months. Methods for measuring the SADT are described in Section 3.4.

1.3.3. Predicting Instability Potential

A general characteristic of self-reactive decomposing chemicals is their inherent "instability" or propensity to decompose. Three indicators can be used to point to the likelihood of unstable behavior in a given chemical compound: (a) endothermicity, (b) presence of certain bonds or functional groups common to unstable materials, and (c) stoichiometry and oxygen balance. These three indicators are discussed in Section 3.2.

1.3.4. Deflagration and Detonation of Pure Material

A decomposition reaction can range from a slow, gas-evolving reaction to the detonation of a high explosive. Decomposition reactions, particularly in the liquid phase, generally occur as reactions in the bulk of the material rather than at a reaction front such as in a deflagration (although deflagrations can occur in the liquid phase). It is often possible to provide emergency relief protection for storage vessels handling such materials, although multiphase flow must usually be considered.

On the other hand, materials such as high explosives that can decompose at detonation velocities cannot generally be vented or contained. (See Glossary for definitions of *deflagration* and *detonation.*) Hence, safeguards and mitigation approaches will be different depending on the speed of the potential decomposition reaction.

1.3.5. Slow Gas-Forming Reactions

Numerous process incidents have occurred in closed systems where evolution of gas over time has caused pressure to build up in the system to the point of containment failure. The gas can evolve from a slow decomposition or hydrolysis reaction, an accelerating thermal decomposition, or a process upset or side reaction. Bretherick (1990, 1604–1607) provides an extensive list of chemicals and reactive systems that have been reported in the literature as causing gas-evolution incidents.

Slow gas-forming decomposition reactions can occur slowly enough that any heat of reaction can be dissipated to the environment, so that an accelerating thermal decomposition/runaway reaction does not occur. Another possible cause of such incidents is materials that have very small heats of decomposition, but the decomposition with gas evolution is caused by a catalytic impurity or other initiator being present that controls the rate of decomposition. Catalytic decomposition of hydrogen peroxide due to metal or metal oxide contaminants, liberating oxygen into the containment in gaseous form (with obvious amplification of any combustion–oxidation hazard if oxidizable material is present), is a common example of this category of reactions.

1.3.6. Heat of Compression

Thermal energy can be imparted to a reactive material by several mechanisms. In addition to thermal energy possibly coming from the surrounding environment (including external fires, steam leaks, etc.) and from slow reactions for which the heat of reaction is not dissipated, the mechanism of adiabatic compression can also generate thermal energy that is sometimes sufficient to initiate a decomposition reaction. Adiabatic compression arises when a compressible fluid is pressurized such that the pressure–volume (P-V) work done on the fluid is manifest in an increased fluid temperature. The fluid must have a positive Joule–Thompson coefficient for a temperature increase to occur.

As an example, the diesel engine works on the principle of autoignition by heat of compression. Hence, fuels that readily self-ignite are desirable for diesel engine fuels. (Converse behavior is found in the spark-ignition engine, where self-ignition causes engine "knock" and is therefore undesirable, so that fuels which resist pre-spark ignition reactions are favored for spark-ignition engines.)

Adiabatic compression has also been known to initiate decomposition of tetrafluoroethylene gas with atmospheric oxygen present. Adiabatic compression can be caused by such mechanisms as opening of a rupture disk below a relief valve, so that the high-pressure process gas compresses the gas in the space between the rupture disk and relief valve. Initiation of ethylene decomposition by compression mechanisms is discussed by Britton et al. (1986).

The autoignition behavior of gases and mists is highly complex, especially when related to the dynamic conditions in equipment such as an engine.

Similarly, dynamic conditions in process equipment containing possible sources of hot-spot autoignition are very difficult to quantitatively analyze (CCPS/AIChE, 1993), although they may be amenable to computer modeling.

1.3.7. Minimum Pressures for Vapor Decomposition

Decomposition of vapor-phase reactive compounds often requires an elevated pressure for the decomposition reaction to propagate. Adiabatic compression situations, as described in the preceding section, can provide both thermal energy for initiation and an elevated pressure if such a pressure is required for vapor-phase decomposition.

Table 1.6 lists available data on materials that may be stored in bulk quantities and that can decompose in the vapor phase without oxygen present, thus having effective limiting oxygen concentrations (LOCs) of zero when above the limiting pressures indicated. It should be noted that, even though the materials listed in Table 1.6 can indeed decompose in the absence of oxygen, having oxygen present will often result in a more easily initiated reaction, a lower pressure requirement for propagation, and/or a greater energy release rate due to a more energetic reaction.

1.3.8. Shock Sensitivity

The decomposition of *shock-sensitive* materials can be initiated simply by the mechanical energy input of a physical impact or a pressure (shock) wave. When

TABLE 1.6
Minimum Pressures for Vapor Decomposition

Gas or Vapor	*Limiting Pressure at Given Temperature*	*Reference*
Acetylene	~1 atm (101 kPa) at 25°C; depends on container diameter and ignition source	Medard, 1989; Bulletin 680
1,3-Butadiene	unknown; theoretically possible	Medard, 1989
Ethylene	~68 atm (6.9 MPa) at 25°C	Bulletin 680
Ethylene oxide	~300 mmHg (40 kPa) at ~30°C	Union Carbide, unpublished
Hydrazine	12 mmHg (1.6 kPa) at 25°C	Bulletin 680
Methyl acetylene	>4 atm (>400 kPa) at 25°C	Bulletin 680
Propadiene	>2.2 atm (>225 kPa)	Bulletin 680

NOTES: Ethylene oxide limiting pressure is reported as 525 mmHg (70 kPa) in Bureau of Mines Bulletin 680. Numbers in Bulletin 680 are order-of-magnitude accuracy. The T-P ranges for the "unknown" values are probably not industrially important except from the standpoint of fire exposure, plus possibly erroneous literature testaments to their stabilities.

some organic peroxides are said to be extremely sensitive to shock (as well as sparks, friction, heat, light, and other initiating mechanisms), this likely refers to such mechanisms as dropping a tool onto a surface where a shock-sensitive peroxide has been spilled. Table 1.7 gives a list of shock-sensitive materials compiled by the National Research Council.

TABLE 1.7
Shock-Sensitive Compounds[a]

Acetylenic compounds, especially polyacetylenes, haloacetylenes, and heavy metal salts of acetylenes (copper, silver, and mercury salts are particularly sensitive)
Acyl nitrates
Alkyl nitrates, particularly polyol nitrates such as nitrocellulose and nitroglycerine
Alkyl and acyl nitrites
Alkyl perchlorates
Amminemetal oxosalts; metal compounds with coordinated ammonia, hydrazine, or similar nitrogenous donors and ionic perchlorate, nitrate, permanganate, or other oxidizing group
Azides, including metal, nonmetal, and organic azides
Chlorite salts of metals, such as $AgClO_2$ and $Hg(ClO_2)_2$
Diazo compounds such as CH_2N_2
Diazonium salts, when dry
Nitrides (silver nitride, Ag_3N) can form in the reaction mixture from the Tollens' test for aldehydes if it is allowed to stand for some time; this can be prevented by adding dilute nitric acid to the test mixture as soon as the test has been completed)
Hydrogen peroxide becomes increasingly treacherous as the concentration rises, forming explosive mixtures with organic materials and decomposing violently in the presence of traces of transition metals.
***N*-Halogen compounds** such as difluoroamino compounds and halogen azides
***N*-Nitro compounds** such as *N*-nitromethylamine, nitrourea, nitroguanidine, nitric amide
Oxo salts of nitrogenous bases: perchlorates, dichromates, nitrates, iodates, chlorites, chlorates, and permanganates of ammonia, amines, hydroxylamine, guanidine, etc.
Perchlorate salts; most metal, nonmetal, and amine perchlorates can be detonated and may undergo violent reaction in contact with combustible materials
Peroxides and hydroperoxides, organic
Peroxides (solid) that crystallize from or are left from evaporation of peroxidizable solvents
Peroxides, transition-metal salts
Picrates, especially salts of transition and heavy metals, such as Ni, Pb, Hg, C, and Zn; picric acid is explosive but is less sensitive to shock or friction than its metal salts and is relatively safe as a water-wet paste
Polynitroalkyl compounds such as tetranitromethane and dinitroacetonitrile
Polynitroaromatic compounds, especially polynitro hydrocarbons, phenols, and amines

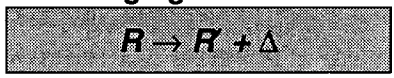
[a]Data from National Research Council, 1983; Shanley and Ennis, 1991.

The importance of shock sensitivity becomes especially acute when considering the possibility of an explosion at one location initiating a more severe decomposition reaction at some distance away from the original location. This potential consequence, as it relates to high explosives, is termed *sympathetic detonation*, and has been extensively studied. Safe separation distances for storage of high explosives in bulk have been determined, and are published as *quantity-distance relationships* in the American Table of Distances for Storage of Explosives (NFPA 495, 1992).

1.3.9. Examples of Shock Sensitivity

In addition to the well-recognized hazards of organic peroxides (NFPA 43B, 1993), other shock-sensitive materials pose hazards to storage and handling operations. For example, traces of unstable materials such as insoluble polyperoxides can accumulate gradually over time until a dangerous concentration is reached. The highly energetic, shock-sensitive compound nitrogen trichloride can be formed when excess chlorine or a chlorinating agent contacts aqueous ammonia, ammonium salts, or a compound containing a hydrolyzable amino-derivative (Bretherick, 1990, 1040). Nitromethane, while not very sensitive, can detonate if sufficient material and a sufficiently energetic stimulus are present.

1.4. Self-Reactive Rearranging Chemicals



Chemicals that are self-reactive by internal molecular rearrangement include those which can liberate energy by isomerizing, disproportionating, or tautomerizing. Although the total risk associated with these types of reactivity is historically small, a few important chemical structures are discussed in this section.

1.4.1. Isomerization

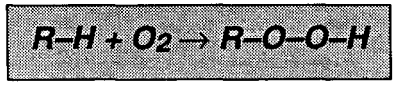
Isomers are different compounds having the same empirical formula, such as ethyl alcohol (CH_3CH_2OH) and methyl ether (CH_3OCH_3) that both have the empirical formula C_2H_6O. Isomerization is the rearrangement of atoms in a molecule, such as a change from a straight chain to a branched molecule. It is employed, for example, in petroleum refining to convert straight-chain to branched-chain hydrocarbons or alicyclic to aromatic hydrocarbons. In some cases, the conversion from a more energetic to a less-energetic isomer can liberate sufficient energy to pose a significant hazard. For example, the conversion of the C_2H_4O isomers ethylene oxide (heat of formation −16.1 kcal/g-mol at 25°C) to acetaldehyde (heat of formation −39.72 kcal/g-mol at 25°C) will liberate 23.6 kcal for each gram mole converted, or 2.24 MJ for each kilogram converted.

One special kind of isomerization occurs with molecular hydrogen, which exists as two "spin isomers" known as *orthohydrogen* and *parahydrogen*. These two distinct forms are possible because two hydrogen atoms may combine with their nuclei spinning in the same (ortho) direction or in opposite (para) directions. These spin isomers are ordinarily fairly stable. However, they may be rapidly interconverted by using a catalyst such as activated charcoal or platinized asbestos. The ratio of the two isomers in an equilibrium mixture varies markedly with temperature. At temperatures approaching absolute zero, equilibrium hydrogen consists entirely of parahydrogen; at room temperature and above, parahydrogen constitutes only 25% of the mixture. Pure parahydrogen may be readily prepared by passing liquid hydrogen over activated charcoal. (Pure orthohydrogen has been prepared only in small quantities.) When ordinary hydrogen is liquefied, the heat evolved during the slow conversion of the equilibrium mixture to parahydrogen is responsible for the evaporation of large amounts of liquid hydrogen during storage (Kaplan, 1982, 6-743). Specific design criteria for storing and handling liquid hydrogen to avoid an explosion or release hazard associated with spin isomerization are given in Section 6.6.

1.4.2. Disproportionation

Disproportionation is a self-reaction in which a compound can form two similar products by transfer of electrons (reduction–oxidation). For example, upon heating, a hypochlorite can yield a chlorate and a chloride. Because most compounds require energy input for disproportionation to occur, such compounds generally do not pose a significant storage and handling hazard except for situations such as an external fire.

1.5. Reactivity with Oxygen



Oxygen-reactive materials have an obvious reactivity hazard due to the ubiquitous presence of atmospheric oxygen. The hazard can translate into a reactive chemical incident either by (a) air getting into the containment that stores or handles the oxygen-reactive material or (b) releasing the oxygen-reactive material into the environment, such as by an accidental spill or release.

If such an oxygen-reactive material does come into contact with air, the ensuing results will be determined by whether the material is *pyrophoric, flammable, combustible,* or *peroxide forming*. The basic characteristics of these and other oxygen-reactive categories are given in Table 1.8. Flammable and combustible materials are not treated in detail in these guidelines.

TABLE 1.8
Categories of Oxygen-Reactive Materials (in general order of decreasing reactivity)

Subset of Oxygen-Reactive Materials	*Basic Characteristics*	*Time Frame of Accident Potential*
Hypergolic	Immediate, spontaneous ignition on contact of fuel with oxidant at ambient conditions; large, extremely rapid energy release	Instantaneous ignition; no additional heat input required
Pyrophoric	Spontaneous ignition in air at or below about 130°F (54.4°C); may require moist air to ignite; large, very rapid energy release	Instantaneous or slightly delayed ignition; no additional heat input required
Low-Temperature Autoigniting	Autoignition temperature above ambient but relatively low (e.g., CS_2, AIT=90-125°C); large, rapid energy release	Immediate or delayed; requires some heat input for autoignition
Flammable	A gas, volatile liquid, or volatile solid with vapors that will burn in air at atmospheric pressure and below 100°F (37.8°C); large, rapid energy release	Immediate or delayed; requires ignition source (e.g., spark, flame, hot surface, or bulk heating to autoignition temperature)
Combustible	Oxygen-reactive gas that will ignite at elevated pressure (e.g., ammonia), liquid with flash point ≥100°F (37.8°C), or oxygen-reactive nonvolatile solid; large, more gradual energy release unless substance is finely divided and premixed with air prior to ignition	Immediate or delayed; requires heat input and ignition source
Autoxidizing	Propensity to slowly oxidize; relatively small energy release (Note: most autoxidation is via peroxide formation)	Ignition source not required for oxidation to occur; can lead to rapid combustion if evolved heat is not dissipated

1.5.1. Spontaneous Ignition and Pyrophoricity

Pyrophoric ("fire-bearing") compounds are highly reactive with atmospheric oxygen and/or humidity, to the extent that contact with the atmosphere causes oxidation and/or hydrolysis at a sufficiently high rate to cause ignition (Bretherick, 1986, 71–72). The criterion for pyrophoricity is not precise, as many materials show pyrophoric behavior under some atmospheric conditions but not others. A working definition is any material that will ignite spontaneously in air,

sometimes with a short ignition delay, under normal conditions of ambient temperature and humidity. Sax and Lewis (1987, 985) give a more precise definition; namely, any liquid or solid that will ignite spontaneously in air at about 130°F (about 54°C). However, gases such as silane can also be pyrophoric.

Pyrophoricity is found in many different classes of compounds, but a few types of structures are notable for this behavior. Examples of pyrophoric materials are given in Table 1.9. A more extensive list that includes less common chemicals can be found in Bretherick (1990, 1778–1781).

Alkylaluminum derivatives (aluminum alkyls) are of particular industrial importance as powerful reducing agents. Literature on these compounds is reviewed by Bretherick (1990, 1492). Compounds with alkyl groups of C_4 and below ignite spontaneously and nearly immediately on exposure to air, unless diluted with a hydrocarbon solvent to 10–20% concentration. Even these dilute solutions may ignite on prolonged exposure to air due to exothermic autoxidation, which becomes rapid if solutions have a high surface-to-volume ratio such as after being spilled. Compounds with C_5 to C_{14} alkyl groups can be handled

TABLE 1.9
Some Pyrophoric Materials

Category	*Examples*
Finely divided metals (without oxide film)	Aluminum, calcium, cobalt, iron, magnesium, manganese, palladium, platinum, titanium, tin, zinc, zirconium
Many hydrogenation catalysts containing adsorbed hydrogen (before and after use)	Raney nickel catalyst with adsorbed hydrogen
Alkali metals	Potassium, sodium
Metal hydrides	Germane, lithium aluminum hydride, potassium hydride, silane, sodium hydride
Partially or fully alkylated metal hydrides	Butyllithium, diethylaluminium hydride, triethylbismuth, trimethylaluminum
Arylmetals	Phenylsodium
Alkylmetal derivatives	Diethylethoxyaluminium, dimethylbismuth chloride
Analogous derivatives of nonmetals	Diborane, dimethylphosphine, phosphine, triethylarsine
Carbonylmetals	Pentacarbonyliron, octacarbonyldicobalt
Grignard reagents (RMgX)	Ethylmagnesium chloride, methylmagnesium bromide
Miscellaneous	Phosphorus (white); titanium dichloride

References: Bretherick, 1986, 71-72; Britton, 1989; Cardillo and Nebuloni, 1992; National Research Council, 1983, 240-241; Sax and Lewis, 1987, 985.

safely at 20 to 30% concentrations. They smoke in air but do not burn unless ignited externally or unless the air is very moist.

Fairly extreme precautions must be taken when storing and handling a pyrophoric material, due to the need for a highly reliable means of keeping the material isolated from the atmosphere. Instead of a fire triangle requiring fuel, air, and an ignition source to have an accidental fire, only the contact of the fuel (pyrophoric material) with the atmosphere is necessary for a fire to occur. Typical handling procedures include storage in tightly closed containers under an inert atmosphere or immersed in a nonreacting liquid and carrying out all transfers and other operations under an inert atmosphere or liquid. Care must be taken to maintain the inerting or diluting material over time, since pyrophoric materials such as metal alkyls in solvents will become more and more reactive as the solvent evaporates. Special precautions must also be exercised in safely disposing of pyrophoric materials such as spent hydrogenation catalysts. Since a further ignition source is not required for combustion of pyrophoric materials, it is not necessary to use electrically classified equipment around such materials (NFPA 70, 1993).

"Low-autoignition materials" are closely related to pyrophoric materials, in that they require only a small amount of heat input to the material in contact with the atmosphere to ignite a combustion reaction. This heat input can come from such sources as heated process equipment or solar radiation. Specific design considerations for pyrophoric and low-autoignition materials are given in Section 6.8.

1.5.2. Pyrophoricity versus Hypergolic Properties

Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances. Accordingly, many pyrophoric compounds can be considered as exhibiting hypergolic behavior. The term is most commonly used, however, to refer to liquid rocket fuels or propellants that consist of combinations of fuels and oxidizers that ignite spontaneously on contact (Sax and Lewis, 1987, 627). The oxidant in a hypergolic mixture does not need to be oxygen.

Presumably, hypergolic behavior is exhibited whenever an oxidation reaction has an extremely low activation energy, such that, at ambient temperatures, as soon as the materials contact each other, the oxidation reaction proceeds rapidly enough to liberate considerable thermal energy and thus propagate the reaction. It would be expected that the reaction rate is, therefore, only limited by the rate at which the reactants are mixed and the product gases can escape. The near-zero activation energy in a hypergolic mixture can be inherent in the particular combination of fuel and oxidizer, or it can be lowered due to catalytic effects such as is the case with hydrogenation catalysts containing adsorbed hydrogen.

The concepts of hypergolic behavior can be extended to other types of reactions as well, such as water-reactive materials. Yoshida (1987, 217–221) describes an apparatus to test for hypergolic ignition by breaking and mixing 500-g reagent bottles and estimating the violence of the ensuing reaction. The test results reported by Yoshida illustrate that some fuel–oxidant combinations may exhibit spontaneous ignition without exhibiting hypergolic behavior (**immediate,** spontaneous ignition). For example, smoking was observed 5 s after mixing and ignition 28 s after mixing when bleaching powder and ethylene glycol were combined. Ignition occurred 2 s after mixing with the combination of sodium chlorite, 60% nitric acid, and toluene.

1.5.3. Accumulation and Explosion of Pyrophoric Materials

Since pyrophoric materials ignite spontaneously in contact with the atmosphere, circumstances of an accidental event do not generally allow accumulation of a large quantity of spilled material prior to ignition. However, a few situations may allow such an occurrence, which could result in a more severe consequence. Among them are the following:

- Some materials are only marginally pyrophoric. For example, they may ignite spontaneously at 125°F with an optimum mixture, but not at normal ambient temperatures. Dichlorosilane is one example of a marginally pyrophoric material.
- Some materials are pyrophoric due to their extremely fast reaction with atmospheric moisture. If the humidity is extremely low, such as outdoors in a desert-type climate or in a heated indoor environment during very cold days, there may be insufficient atmospheric moisture to allow initiation of the combustion reaction.
- Loss of an inert gas purge may allow gradual accumulation of oxygen until a minimum oxygen concentration for ignition is achieved. Accumulation of sufficient humidity in systems that are highly water-reactive can have a similar effect.
- Likewise, loss of an inerting liquid by evaporation or other means may allow eventual exposure of the pyrophoric material to the atmosphere. An example is the handling of Grignard reagents, which are often dissolved in a highly volatile ether that can evaporate if not fully contained.
- Pyrophoric gases such as silane may have effective "flammable limits," such that a minimum concentration may need to accumulate before spontaneous ignition occurs.
- A chemical inhibitor may be present in the system that interferes with the reaction of concern. Depletion of the inhibitor can allow the reaction to begin after an induction period. Some pyrophoric materials may have an

induction period before spontaneous ignition due to other physical/chemical phenomena.

- Formation of a pyrophoric material due to an undesired reaction between incompatible materials can result in the accumulation of sufficient material to pose a significant hazard. Cardillo and Nebuloni (1992) have determined the conditions under which aluminum and halohydrocarbon mixtures will react, with the possible formation of pyrophoric alkylaluminums.
- Pyrophoric iron sulfides (FeS and Fe_2S_3) may form in anaerobic atmospheres in the presence of hydrogen sulfide. They can produce a hot-spot ignition source upon sudden exposure to air (CCPS/AIChE, 1993).
- Finely divided metals such as iron can also ignite upon sudden exposure to air as a result of their large reactive surface areas. Ignition of reduced oxides such as FeO may be possible (CCPS/AIChE, 1993). Other examples are given by Medard (1989).

In each case, it is essential to recognize the hazards of handling the particular pyrophoric material of concern in a specific storage and handling situation. Protection measures can include the detection and warning of (a) approach to an autoignition temperature, (b) presence of moisture, (c) loss of the inerting atmosphere or liquid, and/or (d) the onset of the undesired reaction. In any case, due to the unpredictable nature of pyrophoric behavior (as illustrated in the next section), pyrophoricity itself should not be relied on as a safety feature, such as for preventing the accumulation of hazardous quantities of a material before ignition occurs.

1.5.4. Competition between Air and Atmospheric Moisture

Pyrophoric materials such as some alkylaluminum derivatives react with both the oxygen and the water (humidity) in the atmosphere. The outcome of a spill of such materials will depend on the atmospheric humidity at the time of the spill. The spilled material may burn rapidly under low-humidity conditions, but the same material may smoke away and not ignite under high-humidity conditions. The consequences of such a spill will also depend on the solvent concentration and the volatility of the solvent.

1.5.5. Peroxide Formation

$$R\text{–}H + O_2 \rightarrow R\text{–}O\text{–}O\text{–}H$$

At the other end of the oxygen-reactive materials spectrum from pyrophoric compounds is a group of chemicals that react with atmospheric oxygen much more slowly, but with possibly very hazardous results. This group of chemicals consists of those which can gradually form peroxides. The resulting peroxides can accumulate over time, eventually building up a sufficient concentration to pose a peroxide decomposition hazard.

Peroxide formation, or *peroxidation,* usually takes place slowly when the liquid materials are stored with limited access to air and exposure to light. The peroxides initially formed may subsequently react to form polymeric or cyclic peroxides, many of which are dangerously unstable when concentrated.

The common structural feature in organic peroxidizable compounds is the presence of a hydrogen atom that is susceptible to autoxidative conversion to the hydroperoxy group –OOH. Some of the typical structures susceptible to peroxidation are shown in Table 1.10. (See also Table 2.6 for a list of specific peroxide-forming compounds.) Two or more of these structures within an organic molecule will generally make the compound significantly more susceptible to peroxidation.

Many commonly used chemicals can form peroxides upon exposure to air over a period of time, and some by only brief exposures such as opening a container. A notable example is isopropyl ether (diisopropyl ether), which has been involved in numerous explosion incidents. Storage/handling design and procedures must, therefore, provide highly reliable means to isolate the peroxide-forming material from atmospheric oxygen, detect any dangerous peroxides formed over time, and safely dispose of suspicious inventories. Upon formation, the peroxidized compounds can become particularly dangerous in one of two ways; namely, concentration of the peroxide and initiation of a polymerization reaction. The decomposition of some peroxides is easily initiated and violently explosive in concentrated solution or when dried to a solid; consequently, the evaporation of liquids possibly containing unstable peroxides must be avoided. Sometimes, peroxide-forming solvents, including diethyl ether, tetrahydrofuran, dioxan, 1,2-dimethoxyethane ("glyme"), and *bis*-2-methoxyethyl ether ("diglyme"), are often stored without inhibitors, and are therefore susceptible to peroxidation. Many accidents involving distillation in use of the peroxide-containing solvents have been reported (Bretherick, 1986, 72–73). It is essential to test these solvents for peroxide (such as with sodium or potassium iodide in glacial acetic acid) before use and, if present, peroxides must be eliminated by suitable means before proceeding. Procedures for testing for peroxides and for removing small amounts from laboratory quantities of chemicals are given by the National Research Council (1983, 73–76).

Peroxide formation can also occur in many polymerizable compounds, with the peroxide then capable of initiating an uncontrolled polymerization reaction. Many peroxides are intentionally used as polymerization initiators.

If allyl and, particularly, vinyl monomers become peroxidized, they are potentially dangerous for both of the reasons discussed above. The peroxides of some vinyl monomers such as 1,1-dichloroethylene and 1,3-butadiene separate from solution and are extremely explosive. Even when this does not happen, the peroxide present may initiate the exothermic and sometimes violent polymerization of any vinyl monomer during storage. Reactive monomers must therefore be inhibited against oxidation and stored cool, with regular checks for presence of peroxide. However, contained air should not be completely displaced by nitrogen, as some is essential for effective inhibition (Bretherick, 1986, 72–73).

TABLE 1.10
Some Chemical Structures Susceptible to Peroxide Formation

Structure	*Explanation (NOTE: not all bonds are shown)*
	ORGANIC SUBSTANCES
–O–CH	Ethers and acetals with α hydrogen atoms; especially cyclic ethers and those containing primary and secondary alcohol groups, form dangerously explosive peroxides on exposure to air and light
C=C–CH	Allyl compounds (olefins with allylic hydrogen atoms), including most alkenes
C=C–X	Chloroolefins, fluoroolefins
C=CH	Vinyl and vinylidene halides, esters, ethers, styrenes
C=C–C=C	Dienes (i.e., monomers)
C=CH–C≡CH	Vinylacetylenes with α hydrogen atoms
CH–C≡CH	Alkylacetylenes with α hydrogen atoms
CH–Ar	Tetrahydronaphthalenes, decahydronaphthalenes, alkylarenes with tertiary hydrogen atoms (such as cumene)
CH	Isopropyl compounds; alkanes and cycloalkanes with tertiary hydrogen atoms
C=C–CO_2R	Acrylates, methacrylates
CH–OH	Secondary alcohols
O=C–CH	Ketones with α hydrogen atoms
O=CH	Aldehydes
O=C–NH–CH	Ureas, amides, and lactams that have a hydrogen atom on a carbon atom attached to nitrogen
	INORGANIC SUBSTANCES
Alkali metals, especially potassium, rubidium, and cesium	
Metal amides	
Organometallic compounds with a metal atom bonded to carbon	
Metal alkoxides	

References: Bretherick, 1986, 72–73; National Research Council, 1981, 63–64; National Research Council, 1983, 244–245

1.6. Reactivity with Water

$$R + H_2O \rightarrow P + \Delta$$

Water reactivity is the key type of reactivity of concern for fire protection interests; indeed, a *reactive material* in NFPA 704 (1990) is defined for the purposes of that standard as "one that can enter into a violent chemical reaction with water." (The term *unstable material*, as discussed in Section 1.4, is also used in NFPA 704 with respect to self-reactivity.)

Water is, after air, likely the most common substance other than containment materials to come into contact with reactive materials, even if the contact is unintentional. Since water can have a dilution effect as a solvent and a heat sink, it is usually necessary for a relatively limited amount of water to come into contact with a water-reactive material to give a significant hazard.

Water reactivity can be hazardous by one or more of several mechanisms. The direct heat of reaction may be dangerous to persons or equipment nearby. The violence of the reaction may also cause dispersal of reactive materials. Toxic reaction products such as hydrogen chloride are often formed. Some water-reactive materials evolve flammable gases; for example, potassium, sodium, and many metal hydrides react with water to form hydrogen. The heat of the reaction can often be sufficient to ignite flammable/combustible materials or initiate another type of secondary chemical reaction; for example, the heat of reaction between solid sodium metal and water is sufficient to ignite the hydrogen evolved from the reaction (Yoshida, 1987, 2).

Some concentrated acids or bases can generate considerable heat of dilution when mixed with water. However, this is a physical effect rather than a chemical reaction.

1.6.1. Water Reactivity: Fast and Slow Reactions

Just as there is a broad range of oxygen reactivity (Section 1.6), the intensity with which materials react with water covers a broad range also. Water-reactive materials might be considered in two categories. Some materials react rapidly to violently with water and have an NFPA reactivity rating of 2 or higher based on water reactivity alone. Other materials react relatively slowly but can generate heat and/or gases that can result in elevated pressure if contained. These categories are discussed in more detail in Section 2.5.

1.6.2. Water-Reactive Structures

A list of some typical water-reactive chemical structures is given in Table 1.11. Many of these types of chemicals can react violently with water, especially if the amount of water present is limited. These compounds should always be stored and handled so that they do not come into contact with liquid water or water vapor.

A list of individual chemicals exhibiting water-reactive behavior is presented in Table 1.12. This list was generated by extracting all of the chemicals listed as water-reactive (symbol W) from both NFPA 49 (1994) and NFPA 325M (1994). Ethylene oxide is also included; even though it also is highly reactive and can explosively decompose, it may undergo runaway reaction with water (NFPA 49, 1994). Class B materials react slowly with water, but can build up pressure if confined, possibly rupturing their container.

TABLE 1.11
Some Chemical Categories Susceptible to Water Reactivity (Violent or Slow)

Category	*Examples*
Alkali and alkaline-earth metals	Calcium, potassium, sodium, lithium
Anhydrous metal halides	Aluminum tribromide, germanium tetrachloride, titanium tetrachloride
Anhydrous metal oxides	Calcium oxide
Grignard reagents	Ethylmagnesium chloride, methylmagnesium bromide
Metal alkyls	Aluminum alkyls, lithium alkyls
Metal amides	Lead amide, potassium amide, silver amide, sodium amide
Metal hydrides	Calcium hydride, lithium aluminum hydride, sodium borohydride, sodium hydride
Nonmetal halides	Boron trifluoride, phosphorus trichloride, silicon tetrachloride
Nonmetal halide oxides (inorganic acid halides)	Phosphoryl chloride, sulfuryl chloride, chlorosulfuric acid
Nonmetal oxides	Phosphorus pentoxide, sulfur trioxide
Low-molecular-weight organic acid halides and anhydrides	Acetic anhydride, acetyl chloride
Other	Calcium carbide

References: Bretherick, 1986, 72-73; National Research Council, 1983, 244-245

1.7. Reactivity with Other Common Substances

Some substances are reactive with other common substances besides atmospheric oxygen and water. The hazards of a substance that can react with anything commonly in close proximity to the substance must be identified and carefully controlled. Other common substances can include

- atmospheric nitrogen;
- biological materials;
- concrete, asphalt, wood, and other structural materials;
- metals and other containment materials.

Nitrogen is generally inert to most chemical substances. However, under the proper conditions, it can react violently with lithium, neodymium, or titanium. Extreme precautions must obviously be taken when handling such materials in their pure state. Table 1.13 lists some nitrogen-reactive materials.

TABLE 1.12
Some Materials That React with Water[a]

Water-reactive materials with NFPA reactivity hazard rating of 2, 3, or 4		
Acetyl chloride	Diethyl telluride	Phosphorus pentachloride
Alkylaluminums	Diethylzinc	Phosphorus pentasulfide
Allyl trichlorosilane	Diisobutylaluminum hydride	Phosphorus tribromide
Aluminum chloride, anhydrous	Dipropylaluminum hydride	Phosphorus trichloride
Aluminum phosphide	Ethyltrichlorosilane	Potassium, metal
Amyl trichlorosilane	Ethylaluminum dichloride	Potassium-sodium alloys
Benzoyl chloride	Ethylaluminum sesquichloride	Silicon tetrachloride
Boron tribromide	Fluorine	Silicon tetrafluoride
Bromine pentafluoride	Gallium arsenide	Sodium, metal
Bromine trifluoride	Gallium phosphide	Sodium hydride
Butylacrylate	Germane	Sulfuric acid
Butyllithium	Isophorone diisocyanate	Sulfuryl chloride
Calcium, metal	Lithium, metal	Thionyl chloride
Calcium carbide	Lithium aluminum hydride	Titanium tetrachloride
Chlorine trifluoride	Lithium hydride	Toluene diisocyanate
Chlorosilanes	Methylaluminum sesquibromide	Trichlorosilane
Chlorosulfonic acid	Methylaluminum sesquichloride	Triethylaluminum
Chromium oxychloride	Methyldichlorosilane	Triisobutylaluminum
Diborane	Methyl isocyanate	Trimethylaluminum
Dichloroacetyl chloride	Methyltrichlorosilane	Trimethylchlorosilane
Dichlorosilane	Monochloro-*s*-triazinetrione acid	Tripropyl aluminum
Diethylaluminum chloride	Mono-(trichloro)tetra-(monopotassium dichloro)-penta-*s*-triazinetrione	Vanadium tetrachloride
Diethylaluminum hydride		Vinyl trichlorosilane
Diethyl carbamyl chloride	Phosphorus oxychloride	Zirconium tetrachloride
Examples of materials that react slowly with water		
Acetic anhydride	Butyric anhydride; isobutyric anhydride	Sodium dichloro-*s*-triazinetrione dihydrate
Boron trifluoride	Methylene diisocyanate	Sulfur chlorides

[a]Sources: NFPA 49, 1994; NFPA 325M, 1994.

TABLE 1.13
Some Nitrogen-Reactive Materials[a]

Lithium	Neodymium	Titanium dust	Zirconium dust
Magnesium dust	Thorium dust	Uranium dust	

[a]Sources: NFPA 69, 1992; NFPA 491M, 1991.

Reactivity with surfacing and structural materials are generally well-recognized for a given reactive material. Design and construction considerations will depend on the actual reactive material of concern. Commonly considered here are such hazards as liquid oxygen spills reacting with asphalt to form impact-sensitive explosive mixtures, corrosive materials causing accelerated corrosion and weakening of structural steel, and hydrofluoric acid spills damaging concrete by reacting with the silicon dioxide in the concrete to form silicon tetrafluoride.

1.7.1. Reactions with Metals

Reactivity with metals and other containment materials can take the form of bulk, rapid reaction or slower, corrosive action. Materials of construction must be selected to avoid both immediate and long-term, corrosive reaction between a reactive material and its containment under all normal and foreseeable upset conditions. Few materials will react in bulk with metals used for process equipment; however, there are some notable exceptions. Dry chlorine gas can be handled in iron-based piping under normal conditions, but if a local hot spot exists due to an external fire or other cause, the iron can begin to actually burn due to chlorine being a strong oxidizer. Carbon steel ignites in chlorine near 483°F (251°C). Titanium reacts violently with dry chlorine (CGA, 1990, 314).

Cardillo and Nebuloni (1992) studied the reaction of halogenated hydrocarbons with light metals to form highly reactive metal alkyls. They concluded that there is little evidence of any hazard associated with short-term exposure of bulk metal to halogenated hydrocarbons at ambient temperatures and pressures. However, systems in which light metals such as aluminum are exposed for a prolonged period of time to halogenated hydrocarbons, particularly at elevated pressures and where fresh metal surfaces or metal powders are produced, are susceptible to initiating a violent reaction between the metal and the halogenated hydrocarbon. The referenced article thermochemically evaluated over 2000 binary mixtures of aluminum with several halogenated compounds to identify mixtures with high reactivity. Bretherick (1990, 24–26) reviews 25 other articles on the reactivity of aluminum with halogenated hydrocarbons.

Confinement may make localized elevated pressures possible in such systems. A series of explosions has occurred in recent years with aluminum paint sprayers, when the closing of valves isolated an aluminum part while still in contact with residual paint. Current procedures call for flushing and leaving sprayer valves open.

1.7.2. Surface Area Effects

Reactions with metals and other solids are generally controlled by surface transport phenomena such as diffusion of the reactant or reactants to the metal surface and diffusion of the products from the surface. For this reason, the

amount of surface area exposed to the reactive material has a very strong effect on the outcome of the reaction.

For example, in half of the reported incidents involving reaction of aluminum with halogenated hydrocarbons, aluminum in the form of powder, dust, filings, and turnings was involved. It was concluded that along with temperature and pressure, the physical division of the metal increases its reactivity and any contact of finely divided aluminum with a halogenated hydrocarbon should be viewed with caution (Cardillo and Nebuloni, 1992).

Due to the large surface area and high reactivity of many finely divided metals, intense powdered metal fires, dust explosibility or even pyrophoric behavior can be exhibited (Section 1.6). Active metals with intentionally high surface areas used for such purposes as hydrogenation catalysts are particularly susceptible to high reactivity. Hydrogen adsorbed on the catalyst surface increases the potential severity of incidents involving hydrogenation catalysts.

1.7.3. Catalyst Deactivation and Surface Passivation

Metals having catalytic activity can be deactivated by various contaminants and reactants that either block active sites, alter the chemical or physical nature of the surface, or cause a surface coating to be formed. The surfaces of storage and handling equipment may be intentionally deactivated to prevent catalytic activity from occurring, such as the preparation of a vessel for use in peracetic acid service by passivation of the internal vessel surfaces. The electrochemical, corrosive, and/or catalytic activity of iron, chromium, and related metals can be passivated by treatment with a strong oxidizing agent such as nitric acid or by evolving oxygen onto the surface by electrolysis to form an oxide coating (Sax and Lewis, 1987, 876).

1.8. Reactive with Other Chemicals: Incompatibility

$$A + B \rightarrow P + \Delta$$

There are a virtually unlimited number of possible chemical reactions. However, the combinations that have been involved in hazardous storage and handling incidents are mostly limited to those that produce or lead to an exothermic reaction too large or too fast for effective dissipation under the particular facility conditions (Bretherick, 1986). Besides the self-reactive, oxygen-reactive, and water-reactive chemicals that are emphasized in the preceding sections, quantitative chemical reactions can also result in storage and handling accidents. For example, if a tank truck load of acid is inadvertently unloaded to a tank containing a cyanidic waste, an energetic reaction will ensue and toxic hydrogen cyanide gas will be produced.

Several resources are available to aid in the identification of incompatible materials. The U.S. Environmental Protection Agency has published an extensive list of chemicals in 41 reactivity groups, with expected outcomes for interactions between each group. The document is aimed at incompatibilities related to hazardous wastes (Hatayama et al., 1980). A computerized version of the EPA interaction data is available from Wertz (1989). Bretherick (1990) gives an extensive compilation of incompatibility incidents reported in the literature. An electronic database of Bretherick's data is available from the same publisher. NFPA 491M (1991) is a manual of hazardous chemical interactions based on an extensive literature survey. The use of a *chemical interaction matrix* to systematically identify potentially incompatible mixtures and trace contaminants is detailed in Section 4.1.

Two groups of reactive substances are particularly common: those with oxidizing or reducing properties, and those with acidic or basic properties. These and other important incompatibility potentials are discussed below.

1.8.1. Oxidizing and Reducing Properties

Oxidation–reduction reactions involve the transfer of electrons from one molecule or atom (the one being oxidized) to another (the one being reduced). Oxidizers are electron receptors, and reducing agents (or "fuels") are electron donors. Oxidizers can be considered as solids, liquids, or gases that yield oxygen or other oxidizing gas during the course of chemical reaction or that readily react to oxidize combustible materials. Accordingly, oxidizers include chlorates, perchlorates, bromates, peroxides, nitrates, nitrites, nitric acid, and permanganates. The halogens (fluorine, chlorine, bromine, and iodine), which react similarly to oxygen under certain conditions are, therefore, classed as oxidizers (NFPA 49, 1994). Stull (1977, 5ff) cites specific examples and gives warning that some oxidizers and fuels are less easily recognizable as such, but their combination, nevertheless, results in an energetic reaction.

The rates of oxidation–reduction reactions vary considerably and may be rapid enough to be quite violent. The hazard greatly increases with increasing temperature, and explosive deflagrations are possible under fire exposure conditions. Further, combustible materials that are contaminated or mixed with oxidizers may become sensitive to heat, shock, friction, or impact.

While most inorganic oxidizers such as chlorine gas are not themselves combustible, they can greatly intensify a fire in which they become involved by speeding the oxidation of the burning material. They may also play a role, through their increased concentration, in aiding ignition in air. Small traces of solid oxidant can, in some cases, cause fuels to ignite at room temperature. For example, a mixture of glycerol with potassium permanganate will ignite, though after some delay. Liquid oxygen (or air) can be condensed by very cold equipment such as in liquid nitrogen or helium service. This can be a hazard outside the equipment if liquid air condenses and mixes with a combustible material. Inside

equipment, a hazard can result from traces of oxygen in an inert stream should this condense out (CCPS/AIChE, 1993).

Most of the oxidation–reduction reactions involve a compound that is capable of being oxidized plus air as the most likely oxidizer (see Section 1.6), although many other oxidizers are possible. For example, glycerol reacts vigorously with solid potassium permanganate as the oxidizer. Also, ethanol undergoes violent or explosive oxidation in excess concentrated nitric acid; this reaction involves formation of the unstable compound fulminic acid.

Other oxidation–reduction reactions involve a recognized reducing agent in contact with a material capable of being reduced. For example, a heated mixture of aluminum powder and a metal sulfate will explosively decompose, and sodium in contact with chlorinated solvents is shock-sensitive. Stull (1977, 5) gives examples of non-obvious fuel–oxidant mixtures such as lead chromate, a yellow pigment, and ferric ferrocyanide, a blue pigment.

The most hazardous interactions are between a strong oxidizer and a strong reducing agent. Bretherick cites a severe explosion upon attempted reduction of dibenzoyl peroxide by lithium tetrahydroaluminate. Hydrazine decomposes explosively in contact with chromium trioxide. Space propulsion and power technology also involve examples of strong oxidation–reduction systems capable of extreme energy release (Bretherick, 1986).

1.8.2. Acidic and Basic Properties

Acids are ionic or molecular species that donate protons (hydrogen ions) in solution. Bases, likewise, are proton receptors. Most acid–base reactions are simply characterized as causing heat generation and gas evolution. Acidic and basic properties of materials are generally easier to identify than oxidizing and reducing properties.

1.8.3. Formation of Unstable Materials

One of the most important types of reactions that do not pose a direct hazard, but rather form unstable, and therefore hazardous, substances is that of peroxide formation, which is discussed in Section 1.6.5. Reactions between incompatible materials often form other unstable materials that are either shock-sensitive or can thermally decompose. For example, the highly energetic, shock-sensitive compound nitrogen trichloride can be formed when excess chlorine or a chlorinating agent contacts aqueous ammonia, ammonium salts, or a compound containing a hydrolyzable amino-derivative (Bretherick, 1990, 1040).

1.8.4. Thermite-Type Reactions

Thermite is a mixture of ferric oxide and powdered aluminum. On ignition by a ribbon of magnesium, the reaction produces a temperature of 2200°C which is

sufficient to melt steel. This is typical of some oxide–metal reactions that provide their own oxygen supply and thus are very difficult to stop (Sax and Lewis, 1987).

Mechanical sparks usually require high impact velocities in order to become incendiary. Exceptions include sparks of special materials used as flints in gas lighters, where the hot fragments become incandescent upon reaction with air. Another exception occurs when contacting surfaces react together. The most common of these is reaction between aluminum and oxides such as iron rust or red lead, where the thermite-type reaction may occur. In this reaction, aluminum is oxidized and the iron oxide is reduced, releasing a significant amount of heat. Analogous reactions can occur in other systems of metals and oxides. It is important to recognize that thermite reactions can be hazardous ignition sources even if the metal oxide is present only superficially. The ignition of methane by the impact of an aluminum alloy with a rusty surface has been studied by the Bureau of Mines (CCPS/AIChE, 1993). The use of aluminum with transition metal oxides such as manganese dioxide may lead to explosion (Bretherick, 1990). Thermite-type reactions of aluminum with various oxides of chromium, cobalt, copper, iron, manganese, and nickel are possible.

1.8.5. Incompatibility with Heat Transfer Fluids and Refrigerants

The storage and handling of reactive materials often involves the use of heat transfer fluids for either heating or refrigeration of the material. Heat exchanger tube leaks and other means of mixing heat transfer fluids with reactive materials can lead to serious incidents if the substances are incompatible. Some potential incompatibilities include:

- water with water-reactive materials
- ammonia with acids, halogens, oxidizing materials, etc.
- biphenyl–biphenyl oxide heat transfer fluids in the presence of sulfuric acid or air (sulfonation or oxidation possible)
- chlorofluorocarbon refrigerants with alkali- and alkaline-earth metals; for example, dichlorodifluoroethane (refrigerant-12) with aluminum (Schwab, 1971)
- Coastal Chemical HITEC® oxidizing heat transfer salt mixture containing potassium nitrite, sodium nitrite and sodium nitrate, with fuels and other materials capable of being reduced.

Incompatibilities with alternative refrigerants, particularly various hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), will need to be examined closely as the use of these materials is expected to increase.

1.8.6. Adsorbents

Adsorption is the physical or chemical adherence of atoms, molecules, or ions in any phase to the surface of a solid or liquid called the *adsorbent*. Finely divided

or microporous materials, which, therefore, present a large area of active surface, are strong adsorbents; examples include activated carbon, activated alumina, and silica gel.

Adsorbents may be used in storage and handling operations for such purposes as drying or collection of off-gases. Adsorbents can pose subtle but significant hazards when used in operations handling reactive materials. For example, an adsorbent may serve to catalyze the decomposition of an unstable material in the liquid or gaseous state. Also, the heat of adsorption in a dryer or other unit operation can be high enough to pose a thermal hazard by heating the bulk of the reactive material or by reaching the autoignition temperature of the off-gas vapors. This may be particularly true during process upsets that may, for example, admit impurities into the adsorption unit or cause a high flow rate of organic vapors to pass through the unit.

It can be seen that temperature monitoring of the adsorption unit is an important provision for safe operation. To be effective, such monitoring must measure the actual bed temperature and not just the wall temperature. Britton et al. (1986) and Britton (1994) discuss bed temperature monitoring, as well as the initiation of ethylene decomposition by the heat of adsorption in an adsorbent bed. Purging and pre-loading procedures are also discussed.

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